



TITLE:

# <Division of Multidisciplinary Chemistry>Molecular Aggregation Analysis

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# Division of Multidisciplinary Chemistry

## – Molecular Aggregation Analysis –

URL: <http://www.em2.kuicr.kyoto-u.ac.jp/index.html>



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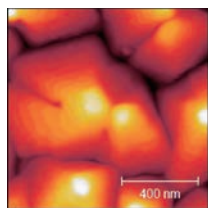
### Scope of Research

The laboratory explores the electronic and photo-electronic properties of organic semiconductor thin films, examining how the physics of charge generation and transport reflects the precise and intricate way molecules assemble, orient, and order in the solid state. Characterization of film growth and studies on the influence of environmental variables on the film structure are combined with *in situ* electrical conductance and photoconductivity measurements. The experimental conditions are carefully controlled to discover new details about charge injection and transport, charge generation, and intermolecular electronic interactions.

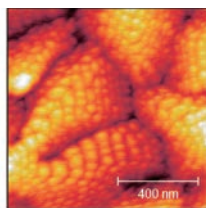
#### KEYWORDS

Organic Semiconductor  
Molecular Electronics  
Thin Films  
Electrical Conductivity and Photoconductivity  
Charge Generation and Transport

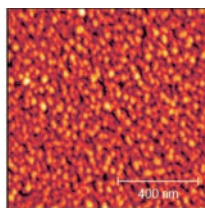
1  $\mu\text{m}$   $\times$  1  $\mu\text{m}$  AFM images of thin organic films grown on silicon wafers.



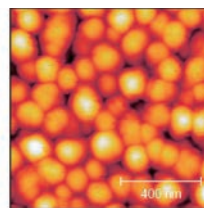
10 nm pentacene



10 nm pentacene  
+ 10 nm C<sub>60</sub>



10 nm C<sub>60</sub>



10 nm C<sub>60</sub>  
+ 10 nm pentacene

### Selected Publications

- Murdey, R.; Katoh, K.; Yamashita, M.; Sato, N., Thermally Activated Electrical Conductivity of Thin Films of Bis(phthalocyaninato)terbium(III) Double Decker Complex, *Thin Solid Films*, **646**, 17-20 (2018).
- Murdey, R.; Sato, N., Photocurrent Action Spectra of Organic Semiconductors, *Advances in Organic Crystal Chemistry Comprehensive Reviews 2015*, 627-652 (2015).
- Murdey, R.; Sato, N., Interpretation of the Thermal Activation Energy of Conduction for Molecular Semiconductor Thin Films with Blocking Contacts, *Jpn. J. Appl. Phys.*, **53**, 05FY04 (2014).
- Murdey, R.; Sato, N., Voltage Stress Induced Reversible Diode Behavior in Pentacene Thin Films, *J. Chem. Phys.*, **137**, 234703 (2012).
- Murdey, R.; Sato, N., *In Situ* Conductance Measurements of Copper Phthalocyanine Thin Film Growth on Sapphire [0001], *J. Chem. Phys.*, **134**, 234702 (2011).

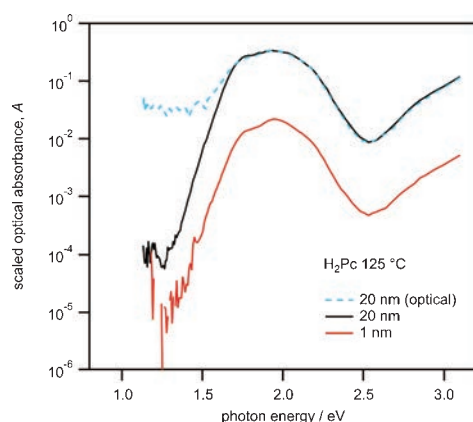
## Nonlinear Photocurrent Spectroscopy

As photocurrent is proportional to the quantity of absorbed radiation it is possible in principle to extract an optical absorption spectrum using the photocurrent recorded at different wavelengths. Photocurrent in this instance can be considered as a measure of the absorbed light. If the relationship between photocurrent,  $I$ , and the absorbed light intensity,  $F$ , is not linear, however, the incident light intensity for each data point must be attenuated such that the photocurrent remains constant – unless a mathematical function can be found to transform the photocurrent into a linear function of absorbance. We have determined that this linearization function, called the current response function, can be expressed as,

$$A = -\log \left( 1 - \frac{1}{Y} \frac{I}{eF} \left( \frac{I}{I_d} + 1 \right)^{\frac{1-\gamma}{\gamma}} \right).$$

$Y$  is a scaling parameter, while  $I_d$  and  $\gamma$  may be determined by a simple fitting procedure. The expression appears to be generally valid for most organic semiconductor films.

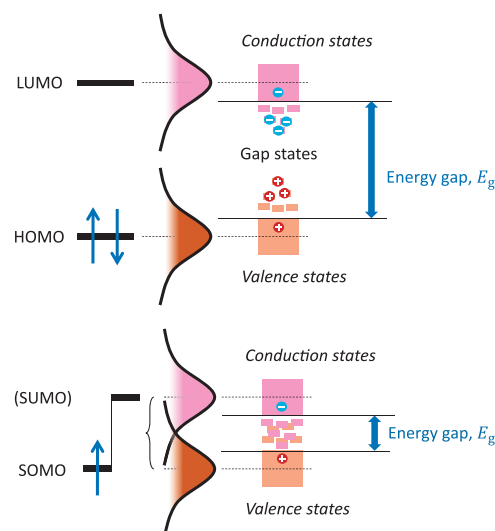
This new technique is called Nonlinear Photocurrent Spectroscopy (NPS). Absorption spectra can be quickly and easily obtained for thin and irregular shaped films, even on nontransparent substrates. There is no need to adjust the incident light intensity for each wavelength. Since NPS has very high sensitivity, the method is well-suited for examining gap states and impurity states in organic semiconductors, as well as for studying very thin films down to a single monolayer. A demonstration of this sensitivity is shown in Figure 1.



**Figure 1.** Absorbance spectra of 20 nm and 1 nm free base phthalocyanine thin films derived from photocurrent measurements after application of the nonlinear current response function and scaled to an optical reference. The reference optical spectra for the 20 nm film measured with the transmitted beam intensity (dotted blue line) is also shown.

## Conductance in Organic Radical Solids

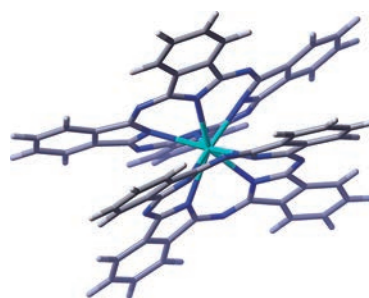
Organic radical molecules are distinctive for their singly occupied molecular orbital (SOMO) which causes them to behave as narrow gap intrinsic semiconductors in the solid state.



**Figure 2.** The relation between the molecular orbitals and the solid state energy gap  $E_g$  in a) typical closed shell organic semiconductors, and b) open shell organic radicals. Charge held in gap states is said to be “trapped”.

Radical bisphthalocyaninato complexes are open shell organic radical compounds which combine high electrical conductivity with chemical and thermal stability, making them promising materials for studying the charge transport of organic semiconductors. The small energy gap effectively removes the influence of deep traps, greatly enhancing the response time and facilitating reliable measurements.

In recent work we have shown that the conductance equation of  $\text{TbPc}_2$  thin films may be separated into exponential and linear terms in temperature. The energy gap is found by this method to be 0.316 eV.



**Figure 3.** Molecular structure of the phthalocyanine sandwich complex bis(phthalocyaninato)terbium(III) ( $\text{TbPc}_2$ ). A single unpaired electron is shared between the two phthalocyanine ligands.